

TID-1-N₂(O₂): selective for NITRO, OXYGENATED, or HALOGENATED compounds

Equipment:

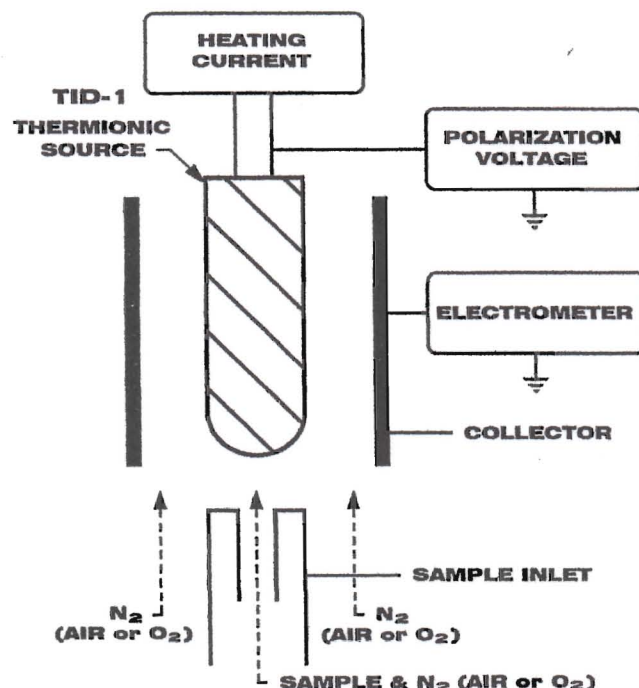
This detection mode uses a TID-1 type thermionic source mounted in either a TID/FID, REMOTE FID, FTID, PTID, or TANDEM TID tower. The detector gas is N₂ flowed through the gas lines which normally provide "H₂" and "air" to an NPD or FID. (Air or O₂ are other possible choices for the detector gases.) The source is heated by a constant current supply and is polarized at -45 Volts relative to the collector. In most applications, the surface temperature of the source is in the range of 400-600 °C which has no visible glow.

Principle:

This mode uses a low work function surface operated in an inert (or oxidizing) gas environment. The surface functions as a reservoir of electrons. Samples impact the surface and are ionized by a process involving the extraction of electrons from the surface. Gas phase negative ions are formed and collected for the detector signal. The process is extremely selective to compounds containing electronegative functional groups such as the NO₂ group, halogen atoms, or oxygenated functionalities. In some cases there occurs a direct electron attachment to the intact sample molecule. In many other cases, there occurs a dissociative electron attachment to an electronegative fragment of the sample molecule. The manner in which electronegative groups are bound in the structure of the sample molecule strongly influences the response.

Response:

This mode is characterized by primary, secondary, and tertiary levels of response. Primary compounds are detectable at femtogram levels and have selectivities of 10⁸ versus hydrocarbons. Examples of primary compounds are 4-nitrophenol, 2,4-dinitrotoluene, TNT, methyl parathion, pentachlorophenol, and heptachlor.



Secondary compounds are detectable at picogram levels and have selectivities of 10⁷ - 10⁵. Examples of secondary responders are atrazine, 2-nitrophenol, 2,4-dichlorophenol, diazepam, chlordane, dieldrin, phenols, carboxylic acids, glycols, vanillin, and methyl salicylate. Tertiary compounds are detectable at 1 - 10 nanogram levels and have selectivities of 10⁴ versus hydrocarbons. Examples of tertiary compounds are alcohols, ketones, aldehydes, phthalates, thiols, and the pyrrole functional group.

The TID-1 source can also be used in oxidizing detector gas environments such as air or O₂. The presence of O₂ in the detector reduces the response of some compounds, and enhances others. Examples of compounds which are enhanced are 2,4-dinitro-phenol, endrin, simazine, furan, and water vapor.

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IIIA. OPERATION: TID-1-N₂ MODE

1.) BASIC DESCRIPTION

In this mode of operation, a thermionic source (TID-1) of very low work function is operated in a chemically inert gas environment of N₂. Sample compounds are ionized by a surface process involving the extraction of electrons from the heated source and the subsequent formation of gas phase negative ions from the sample compound. This mode of operation is extremely specific to compounds which contain electronegative functional groups. In particular, very large responses (femtogram and picogram detectivity) are obtained for certain compounds containing the nitro (NO₂) group and for some polychlorinated compounds. Lower levels of response (nanogram detectivity) are obtained for many oxygenated compounds such as alcohols and phenols. The manner in which the electronegative groups are bound up in the structure of the sample molecule also has a strong influence on the magnitude of response that is obtained. This mode of operation exhibits its greatest specificity when the source is operated at relatively low source heating currents. As the heating current is increased, some responses are obtained for a wider variety of compounds, although the detector still discriminates strongly against many classes of compounds.

2.) DETECTOR GAS FLOWS

In this mode of operation, N₂ is used for both detector gas 1 and gas 2. The principal function of the detector gases is to maintain a well purged detector volume. A flow rate of 10 - 15 mL/min for detector gas 1 generally suffices, while a flow rate of 50 - 70 mL/min is generally adequate for detector gas 2. N₂ is the preferred GC carrier gas, although He can also be used subject to the considerations described on page I-4.

To minimize excessive jet effects at the small orifice of the sample conduit, the sum of the GC carrier gas and detector gas 1 should normally be less than about 40 mL/min. Gas flows are measured at the exit tube of the detector tower using the flow measuring tubing and fitting that are supplied. (On HP 5890 GC installations, gas flows may be more accurately measured at the detector base before installing the detector tower.)

3.) OPERATION

- a.) To become familiar with the response characteristics of the TID-1-N₂ mode, some initial experimentation with high responding test samples is recommended. Examples of good test sample compounds are methyl parathion or 2,4 dinitrotoluene at concentration levels of about 1 - 10 ng. A good source of methyl parathion is Varian TSD test sample #82-005048-04, and a good source of 2,4 dinitrotoluene is 100:1 dilution of Supelco nitroaromatic mixture #4-8742.
- b.) Each new TID-1 source is accompanied by a chromatogram of the response of that source to a test sample. The conditions associated with this chromatogram provide a good starting point for examining the source.

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c.) **GENERAL OPERATING PROCEDURES**

- 1.) Set detector and carrier gas flows in accordance with guidelines in I.I and IIIA.2.
- 2.) Set the detector heater block at the desired operating temperature. (300°C or higher is generally preferred for this detector.)
- 3.) Connect the DET electrometer or the electrometer on the GC to a signal recording device (ie., integrator or data system) and disengage any electrometer autozeroing if applicable. In initial setup of the TID, it is helpful to monitor the magnitude of the background signal level as the source heating current is increased. Set the electrometer and data system attenuations and range so the recorded display corresponds to approximately 10^{-11} Amps for full scale signal.
- 4.) On the DET Current Supply providing heating current to the thermionic source, set the bias voltage switch on the back of the supply at -45 V.
- 5.) With the Current thumbwheel switch initially set at 0000, turn on the Current Supply. The magnitude of heating current required depends on the operating temperature of the heated detector base, and the thermal gradients in the detector hardware depend to some extent on which GC model is used. Typical heating currents are as follows:

Temperature - - - - Heating Current - - - - -

	VARIAN 3800	Ag 6890/NPD	HP5890/6890 FID
100°C	2.7 - 3.0 Amps	2.6 - 2.8	2.9 - 3.1
200°C	2.5 - 2.7 Amps	2.4 - 2.6	2.7 - 2.9
300°C	2.3 - 2.5 Amps	2.2 - 2.4	2.5 - 2.7

Start at the lower end of these ranges and observe the recorded baseline for an indication of signal increase as the heating current is turned up from zero. Typically an initial signal will rise rapidly from the baseline, reach a peak, and then equilibrate to some lower level. The hot thermionic source radiates some heat to the surrounding detector tower, and the equilibration of the detector tower temperature may require as long as 30 minutes. To minimize this thermal equilibration time, set the detector heater block at as high a temperature as allowed by the application so that the thermal gradient between the thermionic source and the surrounding detector wall is minimized.

- 5.) Set the injector and column temperature such that the test sample compounds will have a retention time in the range of 2 - 6 minutes.
- 6.) Inject a volume of about one microliter of the test sample and observe the detector response to the electronegative compounds. Adjust the electrometer attenuation and range if necessary to get an on-scale sample peak and inject the sample again.

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- 7.) Increase the source heating current by an increment of 0.1 Amps and inject the test sample again. Generally, this increase in heating current will increase the magnitude of the background signal as well as the sample response. To ensure on-scale sample peaks, adjust the electrometer range or attenuation to achieve about the same percent of full scale level for the background signal.
- 8.) Response characteristics of interest in these test sample chromatograms are the solvent response, sample compound responses, and magnitude of the detector background signal. Frequently, as the source heating current is increased, the response of the detector to the solvent will increase relative to the sample response. This indicates that the detector becomes less specific at higher currents. Also the ratio of sample peak heights relative to the magnitude of background signal may change with changes in heating current. Generally expect changes in the ratio of sample response to background signal to be indicative of changes in the detector signal-to-noise ratio (ie., detectivity).
- 9.) Compare the two chromatograms of c.6 and c.7 to determine which best suits the desired application of the detector. The following guidelines may be useful:
 - 9.1 Lowest detector noise (ie., about 2×10^{-14} Amps) occurs for background signal levels of 10×10^{-12} Amps or less.
 - 9.2 Highest specificity is obtained at lower source heating currents.
 - 9.3 At some loss of specificity, signal-to-noise ratios (ie., detectivity) can often be improved by increasing source heating current until the detector background signal level reaches about 10×10^{-12} Amps.
 - 9.4 The operating lifetime of the source often decreases with increasing source heating current.
- 10.) Once the preliminary results of c.6 - c.8 have demonstrated the basic characteristics of the TID-1-N₂ mode, the detector is ready to be applied to any analytical sample of interest. Some experimentation with source heating current and/or detector heater block temperature similar to c.6 - c.8 is often helpful to best optimize the detector for each new type of sample.

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IIIAA. OPERATION: TID-1-AIR (O₂) MODE

This mode of operation is similar to the TID-1-N₂ mode, except that the detector gases are Air or O₂ instead of N₂. This mode also is specific for electronegative compounds, but the responses differ from the TID-1-N₂ mode because of the presence of the weakly electronegative O₂ molecule in the gas environment. Generally, the magnitudes of gas flow rates used for detector gas 1 and gas 2 are the same as those recommended for the TID-1-N₂ mode. However, there may be specific applications where the most favorable sample responses are obtained from using detector gas combinations such as Air (O₂) for gas 1 and N₂ for gas 2, or vice versa. Therefore, it is frequently instructive to experiment first with the TID-1 source in an N₂ environment, and then to perform the same analyses with an Air (O₂) environment.

NOTE: Long term operation of the TID-1 source at high source heating currents in an oxygen containing environment sometimes causes a change in the TID-1 surface characteristics such that subsequent operation in an N₂ environment may yield reduced sensitivity. Therefore, once it is established which gas environment is best for a given analysis, the TID-1 source should be dedicated to continued operation in either an N₂ or O₂ environment for best results.

IIIAA-1

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